

**EFFECT OF MOLECULAR WEIGHT AND COMPATIBILIZER ON
MISCIBILITY AND PROPERTIES OF LLDPE/NR BLENDS**



Ms. Parichart Limsila

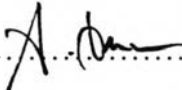
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case western Reserve University
1999
ISBN 974-331-932-8

I 19337514


18 2.A. 2547


Thesis Title : Effect of Molecular Weight and Compatibilizer on
Miscibility and Properties of LLDPE/NR Blends
By : Ms. Parichart Limsila
Program : Polymer Science
Thesis Advisors : Prof. Alexander M. Jamieson
Dr. Rathanawan Magaraphan

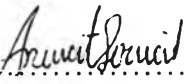
Accepted by the Petroleum and Petrochemical College, Chulalongkorn
University, in partial fulfillment of the requirements for the Degree of Master
of Science.

.......... College Director
(Prof. Somchai Osuwan)

Thesis Committee :

..........
(Prof. Alexander M. Jamieson)

..........
(Dr. Rathanawan Magaraphan)

.......... 10/5/??
(Assoc. Prof. Anuvat Sirivat)

ABSTRACT

##972015 : POLYMER SCIENCE PROGRAM

KEY WORDS : Polymer Blends/Molecular Weight/Linear Low Density
Polyethylene/ Natural Rubber/ Compatibilizer

Parichart : Effect of Molecular Weight and
Compatibilizer on Miscibility and Properties of LLDPE/NR Blends. Thesis
Advisor: Dr.Rathanawan Magaraphan and Prof. Alexander M. Jamieson, 150
pp ISBN 974-331-932-8

The effect of molecular weight (entropic mixing) and compatibilizer (enthalpic mixing) on linear low-density polyethylene (LLDPE) and natural rubber (NR) blends were studied. Maleic anhydride (MA) was added to the LLDPE/NR blends at different concentrations to form *in situ* compatibilizer. The techniques used to determine compatibility were scanning electron microscopy (SEM), differential scanning calorimetry (DSC). The addition of MA to the blends improved the dispersity of the LLDPE/NR blends. A single glass transition temperature (T_g) was obtained for blends with certain amount of MA indicating miscibility of two polymers. T_m and T_c were found to be rather independent of the blend composition and the M_w of NR, but the degree of crystallinity decreased with amount of NR. The blends exhibited enhanced tensile properties with the addition of MA, which was attributed to better adhesion between two phases and the reduction in dispersed particle size. Higher amounts of MA or higher M_w of NR caused reduction in melt flow index (MFI) but improved mechanical properties. The effects of M_w and compatibilizer are compared.

บทคัดย่อ

ปาริชาติ ลิ้มศิลา : ชื่อหัวข้อวิทยานิพนธ์ (ภาษาไทย) การศึกษาอิทธิพลของน้ำหนักโมเลกุลและตัวประสานที่มีผลของการผสมเข้าเป็นเนื้อเดียวกันและคุณสมบัติของโพลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้นตรงที่ผสมกับยางธรรมชาติ (ภาษาอังกฤษ) (Effect of Molecular Weight and Compatibilizer on Miscibility and Properties of LLDPE/NR Blends) อ. ที่ปรึกษา : ศ. อเล็กซานเดอร์ เจมิสัน และ ดร. รัตนวรรณ มกรพันธุ์ 150 หน้า ISBN 974-331-932-8

วิทยานิพนธ์นี้เป็นการศึกษาอิทธิพลของน้ำหนักโมเลกุลและตัวช่วยประสานที่มีต่อผลของการผสมเข้าเป็นเนื้อเดียวกันและคุณสมบัติของโพลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้นตรงที่ผสมกับยางธรรมชาติ โดยการเปลี่ยนแปลงปริมาณความเข้มข้นของมาเลอิกแอนไฮไดรด์ซึ่งทำหน้าที่เป็นตัวช่วยประสานและปริมาณส่วนผสมของโพลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้นตรงและยางธรรมชาติในสัดส่วนที่ผกผันกันจากการศึกษาโครงสร้างของสารผสมโดยใช้เครื่องมือสแกนนิ่งอิเล็กตรอนไมโครสโคป(SEM) พบว่าการเติมตัวช่วยประสานทำให้การกระจายตัวของยางธรรมชาติกระจายตัวดีขึ้นซึ่งบอกให้ทราบว่าการเพิ่มขึ้นของแรงกระทำระหว่างสารทั้งสองที่เนื่องมาจากมาเลอิกแอนไฮไดรด์ และปริมาณที่เหมาะสมของแต่ละสัดส่วนจะแสดงค่าของอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วเพียงจุดเดียว อุณหภูมิการหลอมเหลวและอุณหภูมิการกลายเป็นผลึกไม่ขึ้นอยู่กับส่วนผสมของน้ำหนักโมเลกุลของยางธรรมชาติและสารผสมทั้งสองชนิด จากผลการทดสอบคุณสมบัติเชิงกล พบว่าการเติมปริมาณสารช่วยผสมทำให้คุณสมบัติเชิงกลของสารผสมดีขึ้นเนื่องมาจากการปรับปรุงคุณสมบัติของแรงกระทำระหว่างสารผสมทั้งสองชนิด ในงานวิจัยนี้ยังแสดงผลของคุณสมบัติการไหลและคุณสมบัติเชิงกลโดยการเปรียบเทียบกันระหว่างการเปลี่ยนแปลงน้ำหนักโมเลกุลของยางธรรมชาติและสารช่วยประสานด้วย

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge all professors who have taught her at the Petroleum and Petrochemical College, Chulalongkorn University, especially those in the Polymer Science Program. Sincere thanks Thai Polyethylene Co.Ltd., for providing raw material used in this work.

She greatly appreciates the efforts of her research advisors, Professor Alexander M. Jamieson, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, USA and Dr. Rathanawan Magaraphan of the Petroleum and Petrochemical College, Chulalongkorn University for their constructive criticisms, suggestions and proof-reading of this manuscript. She would like to give thanks to Associate Professor Anuvat Sirivat who give advice and acts as a thesis committee member.

The author also thanks all of her friends and the staff at the PPC who encouraged her in carrying out the experiment and this thesis writing. Finally, the author is also deeply indebted to her mom: Malee Limsila for greatest love, encouragement, and financial support, which give her more encouragement for this research. And for her brother and sister: Sarayuth and Paveena Limsila, the author thanks for everything he and she did for the author.

TABLE OF CONTENTS

		PAGE
	Title Page	i
	Abstract	iii
	Acknowledgements	v
	List of Tables	ix
	List of Figures	xi
CHAPTER		
I	INTRODUCTION	1
	1.1 Polymer Blends	2
	1.1.1 Miscible Blends	3
	1.1.2 Immiscible Blends	3
	1.2 Reactive Compatibilizer as a Compatibilizer for Immiscible Blends	4
II	LITERATURE REVIEW	6
	2.1 Literature Work	6
	2.2 Microstructure	13
	2.3 Research Objectives	17
III	EXPERIMENTAL SECTION	18
	3.1 Materials	18
	3.2 Methodology	22
	3.2.1 Blend Preparation	22

CHAPTER	PAGE	
3.2.2	Determination of % grafting of MA onto LLDPE and NR	26
3.2.3	Molding	27
3.2.4	Melt Flow Index (MFI)	27
3.2.5	Differential Scanning Calorimetry (DSC)	27
3.2.6	Scanning Electron Microscope (SEM)	29
3.2.7	Instron Universal Testing Machine	31
3.2.8	Fourier Transform Infrared (FTIR)	33
3.2.9	Gel Permeation Chromatography (GPC)	33
3.2.10	Vicat Softening Temperature (VST)	34
IV	RESULTS AND DISCUSSION	35
4.1	Materials Characterization	37
4.2	Effect of M_w and Composition on Compatibility and Physical Properties	38
4.2.1	Thermal Properties	38
4.2.2	Morphological Properties	44
4.2.3	Mechanical Properties	48
4.2.4	Vicat Softening Temperature	53
4.3	Effect of Compatibilizer and Composition on Compatibility and Physical Properties	55
4.3.1	Characterization of MA grafting on LLDPE and NR	55
4.3.2	Thermal Properties	61
4.3.3	Morphological Properties	65
4.3.4	Mechanical Properties	71
4.3.5	Vicat softening Temperature	75

CHAPTER		PAGE
	4.4 Effect of NR on Melt Flow Index of LLDPE/NR blends	77
V	CONCLUSIONS	84
	REFERENCES	86
	APPENDIX	93
	A Characterization Data of Molecular Weight	93
	B Determination of Melt Strength	99
	C Thermal Properties Data	101
	D Mechanical Properties Data	105
	E Vicat Softening Temperature (VST) Data	108
	F Possible Reactions of MA onto NR and LLDPE	110
	G Peak Area Data from Fitting Curve Technique	114
	H Melt Flow Index Data	115
	CURRICULUM VITAE	118

LIST OF TABLES

TABLE	PAGE
3.1 Physical properties of LLDPE	19
3.2 Specification for standard thai rubber (STR 5L)	20
3.3 Physical properties of MA	21
3.4 Properties of toluene	21
3.5 Characterization of molecular weight of natural rubber	22
3.6 Dimension of tensile testing specimen as shown in Figure 3.7	32
4.1 Data obtained from GPC to determine molecular weight of LLDPE's	37
4.2 Data obtained from GPC to determine molecular weight of NR	37
4.3 Glass transition temperature of LLDPE/NR ₁₀ blends	38
4.4 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR ₁₀ blends	39
4.5 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR ₂₅ blends	40
4.6 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR ₅ blends	41
4.7 The percent grafting of MA onto LLDPE and NR	59
4.8 Glass transition temperature of blends with compatibilizer	61
4.9 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR ₁₀ blends with various MA concentrations	63
A1 Retention time of standard polystyrene with known molecular weight at 35.2 °C	95
A2 Retention time of standard polystyrene with known molecular weight at 140 °C	97

TABLE	PAGE
C1 Glass transition temperature of LLDPE	101
C2 Glass transition temperature of LLDPE/NR ₁₀ blends	102
C3 Melting temperature, crystallization temperature, degree of crystallinity and heat of fusion data of LLDPE	102
C4 Melting temperature, crystallization temperature, degree of crystallinity and heat of fusion data of LLDPE/NR ₁₀ blends with MA	103
C5 Melting temperature, crystallization temperature, degree of crystallinity and heat of fusion data of LLDPE/NR ₁₀ blends without MA	104
C6 Melting temperature, crystallization temperature, degree of crystallinity and heat of fusion data of LLDPE/NR ₂₅ blends	104
C7 Melting temperature, crystallization temperature, degree of crystallinity and heat of fusion data of LLDPE/NR ₅ blends	104
D1 Mechanical properties of LLDPE	105
D2 Mechanical properties of LLDPE/NR ₅ blends	106
D3 Mechanical properties of LLDPE/NR ₂₅ blends	106
D4 Mechanical properties of LLDPE/NR ₁₀ blends	107
G1 Peak area data of purified and crude of LLDPE	114
G2 Peak area data of purified and crude of NR	114
H1 Melt flow index of LLDPE	115
H2 Melt flow index of LLDPE/NR ₅ blends	115
H3 Melt flow index of LLDPE/NR ₂₅ blends	116
H4 Melt flow index of LLDPE/NR ₁₀ blends	117

LIST OF FIGURES

FIGURE	PAGE
3.1 Chemical structure of LLDPE	18
3.2 Chemical structure of cis-1,4-polyisoprene	19
3.3 Chemical structure of MA	20
3.4 Condition of the twin-screw kneader	24
3.5 Schematic of DSC: (a) configuration of DSC technique; (b) thermogram obtain from DSC	28
3.6 Schematic diagram of a scanning electron microscope	30
3.7 Dimension of tensile testing specimen	32
4.1 Temperature of LLDPE/NR blends	40
4.2 The variation of crystallization temperature of LLDPE/NR blends	41
4.3 The variation of degree of crystallinity LLDPE/NR blends	42
4.4 SEM micrographs of LLDPE/NR ₁₀ blends: (a) 90/10 : LLDPE/NR ₁₀ ; (b) 80/20 : LLDPE/NR ₁₀ ; (c) 70/30 : LLDPE/NR ₁₀ ; (d) 50/50 : LLDPE/NR ₁₀	44
4.5 SEM micrographs of LLDPE/NR ₂₅ blends: (a) 90/10 : LLDPE/NR ₂₅ ; (b) 80/20 : LLDPE/NR ₂₅ ; (c) 70/30 : LLDPE/NR ₂₅ ; (d) 50/50 : LLDPE/NR ₂₅	45
4.6 SEM micrographs of LLDPE/NR ₅ blends: (a) 90/10 : LLDPE/NR ₅ ; (b) 80/20 : LLDPE/NR ₅ ; (b) 70/30 : LLDPE/NR ₅ ; (d) 50/50 : LLDPE/NR ₅	46

FIGURE	PAGE
4.7 Effect of M_w and composition on mechanical properties of LLDPE/NR blends: (a) tensile strength; (b) yield strength; (c) modulus; (d) elongation at break	50
4.8 Morphological model of LLDPE/NR blends for failure phenomena	51
4.9 Effect of composition on vicat softening temperature of LLDPE/NR ₁₀ blends	53
4.10 Grafted MA onto LLDPE	56
4.11 Grafted MA onto NR	56
4.12 FTIR spectrum of MA grafted LLDPE	58
4.13 FTIR spectrum of MA grafted NR	58
4.14 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 90/10 LLDPE/NR ₁₀ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA	67
4.15 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 80/20 LLDPE/NR ₁₀ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA	68
4.16 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 70/30 LLDPE/NR ₁₀ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA	69

FIGURE	PAGE
4.17 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 50/50 LLDPE/NR ₁₀ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA	70
4.18 Effect of compatibilizer on mechanical properties of LLDPE/NR ₁₀ blends: (a) tensile Strength; (b) yield Strength; (c) modulus; (d) elongation at break	73
4.19 Effect of composition on vicat softening temperature of LLDPE/NR ₁₀ blends with various MA	75
4.20 The variation of melt flow index of LLDPE/NR blends	77
4.21 The variation of melt flow index of LLDPE/NR ₁₀ blends with various MA	78
4.22 Comparison the effect of M _w of NR and MA concentration of LLDPE/NR: 90/10 blends on the melt flow index	79
4.23 Comparison the effect of M _w of NR and MA concentration of LLDPE/NR: 90/10 blends on the elongation at break	80
4.24 Comparison the effect of M _w of NR and MA concentration of LLDPE/NR: 90/10 blends on the degree of crystallinity	81
4.25 Comparison the effect of M _w of NR and MA concentration of LLDPE/NR: 90/10 blends on the tensile strength	82
A1 The calibration curve of standard polystyrene in THF At 35.2 °C and flow rate 1.0 ml/min	96
A2 The calibration curve of standard polystyrene in THF At 140 °C and flow rate 1.0 ml/min	98
B1 The picture of melt strength tester as shown by Micic <i>et al.</i> (1996)	100

FIGURE	PAGE
F1 Possible reaction of NR and MA to obtain NR-g-MA: (a) MA present at the middle of NR chain; (b) MA present at the end of NR chain	110
F2 Possible reaction of NR and MA to obtain LLDPE-g-MA: (b) MA present at the middle of LLDPE chain; (b) MA present at the end of LLDPE chain	111
F3 Grafting reaction to obtain graft copolymer of NR and LLDPE with MA linkage (LLDPE-MA-NR): (a) reaction between F1(a) and F2(b); (b) reaction between F1(b) and F2(a); (c) reaction between F1(a) and F2(a)	112
F4 Block copolymer of NR and LLDPE with MA linkage (LLDPE-b-MA-NR)	113